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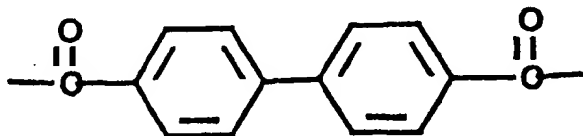


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(54) Title: BIAXIALLY ORIENTED COPOLYESTER FILM PRIMED WITH VINYL ACETATE POLYMERS



(I)

(57) Abstract

The invention concerns a primer coated, biaxially oriented self-supporting mono- or multilayer copolyester film, wherein the copolyester is PENBB and wherein the primer coating contains a vinyl acetate copolymer. PENBB is a copolyester containing units of formula (I).

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## BIAXIALLY ORIENTED COPOLYESTER FILM PRIMED WITH VINYL ACETATE POLYMERS

5 The present invention relates to biaxially oriented copolyester film coated on one or both sides with vinyl acetate polymers which render the copolyester film surface receptive to additional reprographic or matte coatings applied thereto, and to film containing the reclamation product of such coated film.

### 10 Background Of The Invention

Oriented polyester films, particularly biaxially oriented film composed of polyethylene terephthalate (PET), are widely used as a base for drafting film, photographic film, and reprographic film, as well as for packaging and labeling applications.

15 Polyester films, especially PET films, have disadvantages which still need to be overcome, e.g., UV resistance, dimensional stability, heat stability, and hydrolysis resistance are still poor. Moreover, PET film is hydrophobic and is not readily receptive to coating in most applications where the film is to serve as a base or support for other coatings, and must therefore be first coated on one or both sides with a primer coating which adheres to the film and is receptive as well to other coatings applied to it. For example, U.S. Patent Nos. 2,627,088 and 2,698,240 teach a primer coating for PET film comprising a terpolymer composition of vinylidene chloride, acrylic ester and itaconic acid. This primer layer is said to have excellent adhesion to the polyester surface and to water or alcohol based photographic gelatin layers subsequently coated thereon.

25 Another known PET film primer includes copolymers of a vinyl halogenoester, such as vinyl chloroacetate which may be copolymerized with numerous different monomers such as acrylic and methacrylic acids, esters and amides, olefins and vinyl alcohols as disclosed in U.S. Patent No. 3,674,531. Such copolymers may also be crosslinked by the inclusion of melamine or urea formaldehyde resins in the composition. The primed PET

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film is stated to exhibit enhanced adhesion to a variety of coatings applied thereto, including reprographic coatings.

While some of these and other polyester film primer layers are effective in enhancing the adhesive qualities of PET film, it is important for the film manufacturer that scrap film made during production must be recyclable. 5 through the film-forming process. Scrap film is normally comminuted, melted, extruded into the form of pellets, mixed with fresh virgin polyester, re-melted and re-fed to the film-forming extruder. Typically high temperatures may be encountered during such processing of PET reclaim film. Many of the primer compositions discussed above are not stable at such temperatures and 10 tend to impart an undesirable yellow or black discoloration to finished oriented PET film containing significant amounts of such primed reclaim film, particularly after repeated passes through the extruder. Such is the case with the vinylidene chloride-containing polymers used as PET primer layers and disclosed in U.S. Patent Nos. 2,627,088 and 2,698,240. It is also the case 15 with primer layers based on copolymers containing vinyl chloroacetate as disclosed in U.S. Patent No. 3,674,538. It has been found that discoloration and degradation of these primer layers during the reclaim process is most likely attributable to the evolution of chlorine gas or hydrogen chloride in the case of chlorine-containing primer layers. 20

Another known primer is the thermoset, acrylic or methacrylic coatings taught in U.S. Patent No. 3,819,773, which can be applied to the PET film from aqueous medium. Such a primer layer enhances the adhesion of organic solvent based reprographic and drafting layers applied thereto and also the 25 heat sealability.

British Patent No. B 1,127,076 teaches the application to PET film of a primer layer which may comprise an aqueous latex of non-crosslinked polyvinyl acetate. The patent indicates that such primer layers render the film heat-sealable. British Patent No. 1,146,215 teaches the application to 30 PET film of a primer coating comprising an aqueous dispersion of a copolymer of vinyl acetate (100 parts), alkyl methacrylate (10 parts) and itaconic acid (6 parts). The patent indicates that the primer provides enhanced adhesion to

aqueous based gelatin photographic emulsions, but does not indicate that organic solvent based coatings may be successfully applied thereto. U.S. Pat. No. 3,674,531 discloses the application to PET film of a primer layer comprising a copolymer of a vinyl halogenoester, such as vinyl chloroacetate, which may be copolymerized with numerous different monomers such as acrylic and methacrylic acids, esters and amides, olefins and vinyl alcohol. This copolymer may also be crosslinked such as by the inclusion of a melamine or urea formaldehyde crosslinking agent. The primed PET film is stated to exhibit enhanced adhesion to a variety of coatings applied thereto, including reprographic coatings. U.S. Pat. No. 3,624,021 discloses a matte coating composition for PET film based on a mixture of a vinyl acetate/crotonic acid copolymer and an excess of a urea formaldehyde resin which presumably crosslinks upon the application of heat. British Patent 1,497,657 discloses a similar primer coating for PET film which is based on a mixture of an unhydrolysed polymer or copolymer of vinyl acetate and one or more synthetic resins capable of intra-molecular crosslinking, such as a melamine formaldehyde resin. The patent indicates that the primer layer may serve, inter alia, as an anchor layer for the application of further coatings, such as light-sensitive layers. A similar disclosure is found in U.S. Pat. No. 4,066,820. Other patents disclosing the application of crosslinkable vinyl acetate polymers to various surfaces are found in U.S. Pat. No. 2,553,524 and U.S. Pat. No. 3,307,690.

U.S. Pat. No. 3,720,539 discloses a primer coating system for polyester film comprising a first undercoat based on a composition containing a polyacrylamide or polyvinyl alcohol polymer and having applied over such undercoat a coating comprising a mixture of polyvinyl acetate and a melamine/formaldehyde resin. Although this system adheres well to the film, it is a complicated formulation involving two coating steps and also includes materials such as trichloroacetic acid which are not especially desirable in such coating formulations.

British Patent No. 1,168,171 teaches the application to PET film of a primer layer described as a curable copolymer of an unsaturated aliphatic acid

and at least one other ethylenically unsaturated monomer. The patent indicates that such a primer coating enhances adhesion to aqueous based gelatin photographic emulsions, but does not indicate that organic solvent based coatings may be successfully applied thereto. This patent also discloses that film primed with the vinyl acetate coatings described therein may be reclaimed in the film forming extruder by mixing it with 50 percent by weight or more of virgin polyester and refeeding the mixture to the film-forming extruder. This reference discloses that problems of discoloration or degradation caused by certain prior art primer coatings are reduced. While this is true in comparison with the chlorine-containing primers discussed above, the vinyl acetate primer coatings of this patent, which are crosslinked using the resinous crosslinking agents disclosed therein, still are found to give rise to an undesirable yellowing of finished film containing such primed film as reclaim, particularly when compared to film based solely on virgin polymer.

#### Summary Of The Invention

It has now been found that a primer coated biaxially oriented self-supporting mono- or multilayer copolyester film, wherein the copolyester is PENBB and wherein the primer coating contains a vinyl acetate polymer provides excellent UV resistance, good dimensional stability, heat stability and hydrolysis resistance, lower moisture absorption, improved stiffness (tensile modulus) and tensile strength, while providing excellent adhesion to many organic solvent based coatings subsequently applied thereto, and reclaimability when reprocessed during the manufacture of the PENBB film without giving rise to hardly any appreciable degradation of the film.

Many of these coatings are disclosed for PET film in U.S. Patent No. 4,592,953.

U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolyesters, however, biaxially oriented PENBB films are not disclosed or envisioned. In particular, those films with improved stiffness

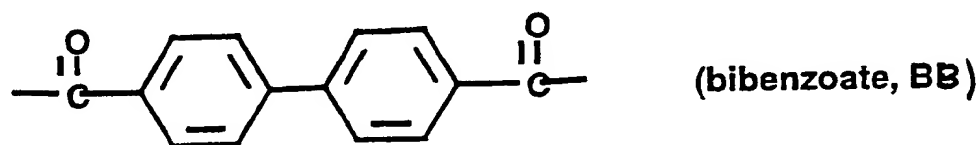


(tensile modulus) and tensile strength in both MD and TD as well as thermo-stability, UV stability, hydrophobicity, dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

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#### Description Of The Preferred Embodiments Of The Invention

PENBB as mentioned hereinbefore is a copolyester containing as acid-derived unit at least 5 mole percent of a radical of the formula



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In the case that more than 10 mole percent of terephthalic acid derived radicals are present in the copolymer, the content of bibenzoate derived units is at least 25 mole percent. Films of these copolyesters are mentioned in the unpublished German Patent Application P 4224161.8, which is incorporated herein by reference. Preferably PENBB is a copolyester wherein at least 80 mole percent of the acid derived units (NBB) consist of bibenzoate (20 to 80 mole percent, preferably 40 to 60 mole percent) and naphthalate (80 to 20 mole percent, preferably 60 to 40 mole percent). The remaining 20 or less mole percent may consist of other acid derived units, which e.g. affect the melting point or the crystallization kinetics. Preferably at least 80 mole percent of the diol-derived units consist of  $-O(CH_2)_2-O-$  units. The remaining 20 or less mole percent consist of other diol-derived units, which e.g. may also affect the melting point or the crystallization kinetics. It may also be desirable to replace minor amounts of the acid- and/or diol-derived units with hydroxycarboxylic-acid-derived units, e.g. such derived from p-hydroxybenzoic acid.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, is then biaxially oriented, heat set, optionally post treated and wound on a roll. In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV

value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g. For a multilayer film known methods for coextrusion, in-line or off-line coating can be used. The solidified film as extruded on the chill roll should be obtained in a essentially amorphous state. To achieve this, the melt film must be pinned to the chill roll by a known method such as electrostatic pinning or vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine (MD) and transverse direction (TD). This stretching can be either simultaneous or sequential. In the case of sequential stretching the first stretching step can be in either MD or TD, followed by stretching in the other direction. The orientation in MD can also be achieved in several steps, either one after another prior to stretching in TD, or before and after the TD stretching. Preferred temperatures for stretching lie between the glass transition temperature and about 30°C above the cold crystallization temperature of the PENBB copolymer composition in use (both temperatures can easily be measured on amorphous films by DSC). The total stretch ratios ( $\lambda$ ) in MD and TD lie between 1 : 2 and 1 : 10, preferably between 1 : 2.5 and 1 : 5. The product of the total stretch ratios should be between 1 to 30 preferably between 5 to 20. Biaxial drawing is performed such that the birefringence is < 0.2, preferably < 0.1 to ensure adequately isotropic properties. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

In order to optimize properties, such as shrinkage, relaxation steps can be included in the orientation and heat setting processes.

The heat setting takes place at a temperature between the cold crystallization temperature and the melt temperature of the copolymer composition.

In some cases a surface treatment such as corona, plasma or flame treatment should be employed before winding the film on a roll.

Prior to coating the copolyester film surface with the acetate coating composition, the film may be surface treated in a conventional manner by exposure to, e.g. an electric corona, plasma or flame treatment. Electric corona discharge is a conventional surface treatment which is commonly performed on a film to enhance its surface qualities, especially its adhesive and printing properties. Electric discharge methods and apparatus are described in U.S. Patent Nos. 3,057,792 and 4,239,973. If the surface treatment followed by the coating occurs before stretch orientation, heating the film before stretch orientation will drive off the water. For biaxially oriented film, preferably the corona treatment followed by the acetate polymer coating may occur during the in-line manufacturing process, either before stretch orientation, or between the machine draw and transverse draw of biaxial stretch orientation, or after stretch orientation. If the surface treatment and coating steps occur after stretch orientation, it is necessary to completely dry the film before winding. If the surface treatment and coating occur before orientation, or between draw during orientation, the later orientation steps which require the film to be heated would drive off the excess water from the acetate polymer coating. Preferably, for biaxially oriented film the corona treatment and subsequent acetate polymer coating occur between draws during the stretch orientation step.

The mono- or multilayer PENBB film is coated on the corona, plasma or flame treated surface preferably with an aqueous dispersion of the acetate coating composition described below. The coating composition may conveniently be applied as an aqueous dispersion or emulsion using any of the well known coating techniques. For example, the film may be coated by roller coating, spray coating, gravure coating, or slot coating. The heat applied to the film during the subsequent pre-heating, stretching, and heat setting stages is generally sufficient to evaporate the water and crosslink the acetate coating, if a crosslinkable monomer comprises a portion of the acetate coating.

The coated, biaxially oriented PENBB film may then be heat treated for a period of time necessary to crystallize the film. Crystallization imparts the

improved dimensional stability and excellent tensile properties to the PENBB film. The so coated crystallized, biaxially oriented PENBB film is then wound onto a roll.

5 The above description deals with an aqueous vinyl acetate coating applied in-line (during manufacture). While this is the preferred process for the biaxially oriented PENBB film, organic solvent-based vinyl acetate coatings as well as off-line coating (after manufacture of the film is complete) is a further aspect of the invention.

10 The vinyl acetate copolymers used as primer layers consist essentially of at least about 50% by weight of polymerized vinyl acetate, which is unhydrolyzed or less than 25% hydrolyzed, and from about 1% to 15% by weight of a copolymerizable comonomer which in its copolymerized state is then capable of inter-molecular crosslinking by the application of heat without the addition of a separate crosslinking agent. Examples of such suitable  
15 crosslinking comonomers include N-methylol acrylamide, N-methylol methacrylamide and their corresponding ethers; epoxy materials such as glycidyl acrylate, glycidyl methacrylate and allylglycidyl ether; carboxyl containing materials such as crotonic acid, itaconic acid or acrylic acid; anhydrides such as maleic anhydride or itaconic anhydride; hydroxy containing monomers  
20 such as allyl alcohol and hydroxy ethyl or propyl acrylate or methacrylate; amides such as acrylamide, methacrylamide or maleamide; and isocyanates such as vinylisocyanate or allylisocyanate.

Preferred comonomers from the above are N-methylolacrylamide and N-methylolmethacrylamide, mainly because copolymer chains containing one  
25 of these monomers are capable of condensing with one another with the application of heat to form the desired inter-molecular crosslinking. In the case of copolymers containing the other functional monomers, it is necessary to form blends of two or more copolymers containing different functional comonomers to achieve the desired crosslinking, e.g. blending a vinyl acetate/  
30 crotonic acid copolymer with a vinyl acetate copolymer containing isocyanate, epoxide or N-methylol functionality capable of reacting with acidic functional groups.

Specific additional combinations of such blended vinyl acetate copolymers include copolymers containing monomers having epoxide functionality combined with copolymers containing monomers having amine, acid anhydride, carboxyl, hydroxyl or N-methylol functionality; copolymers containing monomers have N-methylol or N-methylol ether functionality combined with copolymers containing monomers having carboxyl, hydroxyl, or amine functionality; copolymers containing monomers having isocyanate functionality combined with copolymers containing monomers having carboxyl or hydroxyl functionality; and so forth. Preferably, the functional monomers present in the mixed copolymer systems are present in approximately equimolar amounts.

The vinyl acetate copolymers also may contain up to about 49% by weight of one or more halogen-free monoethylenically unsaturated monomers interpolymerized therewith. Suitable comonomers include dialkyl maleates such as dioctyl maleate, di-isooctyl maleate and dibutyl maleate; vinyl esters of versatic acid; styrene and styrene derivatives; acrylics such as ethyl acrylate and 2-ethylhexylacrylate; acrylonitrile and similar materials.

The preferred crosslinking mixed copolymer compositions for the purposes of this invention are approximately 50/50 blends of a vinyl acetate/crotonic acid copolymer (99-85:1-15 monomer weight ratio) with vinyl acetate/glycidyl acrylate copolymer (99-85:1-15 monomer weight ratio); blends of a vinyl acetate/methacrylamide copolymer (99-85:1-15 monomer weight ratio) with a vinyl acetate/N-methylolacrylamide copolymer (99-85:1-15 monomer weight ratio); and compositions containing non-mixed copolymers based on copolymers of vinyl acetate with N-methylol acrylamide such as copolymers containing from about 50 to 99% by weight vinyl acetate, 0 to 49% by weight of the mono-ethylenically unsaturated monomer and about 1 to 15% by weight N-methylolacrylamide. More preferred are copolymers containing from more than about 50 up to 90% by weight vinyl acetate, about 5 to 45% by weight of the mono-ethylenically unsaturated monomer, preferably methyl methacrylate, and from about 5 to 10% by weight N-methylolacrylamide.

As pointed out above, the polymeric vinyl acetate primer composition does not require the presence of an external crosslinking agent such as a melamine or urea/formaldehyde condensate.

5 The primer coating is applied to the base mono- or multilayer PENBB film preferably as an aqueous dispersion or latex and at a solids concentration within the range of about 0.5 to 15%, preferably about 3 to 10% by weight. The preferred solids level is such as to yield a final dry coating thickness within the range of about 1 to 300 nm, which translates into a solids level on a weight basis of from 1 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>. The preferred thickness  
10 range of the dried copolymer primer is from 15 to 50 nm, with 25 nm being the target thickness. The thickness of the base film to which the coating is applied may range from about 10 to about 250  $\mu$ m.

The coating may be applied to one or both sides of the mono- or multilayer PENBB film, or it may be applied to one side only, and optionally a  
15 different coating may be applied to the opposite side. Additives known in the art may be present in the coating formulation such as anti-static agents, wetting agents, surfactants, pH regulating agents, anti-oxidants, dyes, pigments, slip agents such as colloidal silica, and the like. Normally, it is desirable to include an ionic surfactant to enhance the wettability of the  
20 aqueous coating to the base PENBB film thereby further improving adhesion.

PENBB film primed with the above composition has excellent utility as a film base for the production of photosensitive reprographic films. Such films are prepared by forming a coating on a surface of the primed PENBB film of a photosensitive composition comprising an organic solvent solution  
25 of a resinous binder containing or impregnated with a light-sensitive diazonium compound, and drying said coating. Resinous binders suitable for this purpose include cellulose acetate butyrate, cellulose acetate, cellulose acetate propionate as well as vinyl polymers such as polyvinyl acetate. Suitable solvents include acetone, methyl ethyl ketone, methyl isobutyl ketone, ethylene  
30 ne glycol monomethyl ether and mixtures thereof. These reprographic coatings and their method of application and use are well known in the art.

Similarly the primed PENBB film of this invention forms an excellent substrate for the application of matte coatings which render the film suitable for use as a drawing or drafting material. These matte coatings may be based on an organic composition comprising a resinous binder and a finely divided particulate material which serves as a "toothing agent." The resinous binder may include the resinous materials referred to above as well as acrylic or methacrylic resins. The organic solvents may also include those listed above. Particulate materials include finely divided (less than 10  $\mu$ m particle size) clays or silica. Other ingredients such as thickeners or dispersing agents may also be present in such matte formulations. Similar matte formulations are disclosed for example in British Patent No. 1,072,122 and U.S. Patent No. 3,624,021.

Yet another application of the primed PENBB film of this invention is as a packaging or label material. The primed films demonstrate good adhesion to organic solvent based printing inks and markedly improved UV resistance, dimensional stability, stiffness (tensile modulus) and tensile strength when compared with unprimed film, especially unprimed PET film. These inks may comprise organic solvent dispersions or solutions of pigments and/or dyes in combination with acrylic resins or other resins and thickening agents.

Accordingly, the excellent UV resistance, dimensional stability, stiffness (tensile modulus), tensile strength and adhesive qualities of biaxially oriented PENBB film primed with the crosslinked acetate copolymer layers of this invention to organic solvent based coatings applied thereto renders such film of more universal utility to the manufacturer of finished reprographic, graphic and packaging products.

Reprographic adhesion (Repro) is evaluated using a lacquer comprising (in parts by weight) 9 parts cellulose acetate butyrate of "20 second" grade dissolved in a mixture of 88 parts ethylene glycol monomethyl ether (methyl cellosolve) and 3 parts methyl ethyl ketone with Rhodamine B dye added for color (3 parts of a 1 percent Rhodamine B dye in n-butanol). The lacquer is applied to the coated surface of the film by means of a wire-wound bar, Meyer rod No. 70, and cured in an oven for 5 minutes at 60°C. The coating

is scored with a cross-hatched pattern by means of scalpel. A strip of adhesive tape (Scotch tape 610) is adhered to the cross-hatched area, rubbed with a fingernail to insure intimate contact and then pulled rapidly from the film. The amount of lacquer remaining in the cross-hatched area is expressed  
5 as a percentage of the amount remaining, i.e. no lacquer removed = 100 percent adhesion, all lacquer removed = 0 percent adhesion, with intermediate adhesion values being assessed in terms of the proportion of lacquer area remaining adhered to the film. The test is done twice on two sheets (total of 4 areas tested) and the adhesion value reported as that of the test  
10 area showing the most failure.

Repro test results demonstrating less than 95 percent adhesion are not generally considered acceptable, whereas test results approaching or equaling 100 percent adhesion are the target standard.

The mechanical properties are measured in a tensile testing machine  
15 made by Zwick (Ulm, Germany) on 15 mm wide strips of film. The initial distance between the chucks is 100 mm and the crosshead speed is 100 mm/min for the strength and elongation determination and 10 mm/min for the tensile modulus determination.

The UV resistance is tested by measuring the retention of tensile  
20 elongation after exposure to UV light in a "Suntest" apparatus manufactured by Heraeus (Hanau, Germany) for 14 days.

The following example is illustrative of the invention.

#### EXAMPLE

25 A latex comprising 4.5 percent by weight solids of a copolymer of 90 weight percent of vinyl acetate, 5 weight percent methyl methacrylate, and 5 weight percent of N-methylolacrylamide, 0.5 weight percent of colloidal silica, and an anionic surfactant is applied as a primer coating to a PENBB film which is made of 289 parts by weight of dimethyl 2,6-naphthalene dicarbox-  
30 ylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol. Granules of this polymer, having a melting point of 281°C are melted in a single screw extruder at temperatures of 280 to



320°C and extruded through a sheet die onto a cooling roll, which is temperature controlled at 30°C. A 120  $\mu\text{m}$  thick film is obtained which is clear and transparent. Its density is 1.31 g/cm<sup>3</sup>. This pre-film is then sequentially biaxially oriented. The longitudinally drawn film is corona treated by a corona discharge apparatus and thereafter coated with the latex described above by reverse gravure coating. The corona treated longitudinally drawn, coated film is dried at a temperature of about 100°C. Thereafter the film is stretched in the transverse direction. The biaxially drawn film is heat set at a temperature of 230°C. These heat treatments result in the crosslinking of the primer coating.

The thus obtained primer coated film shows the following characteristics compared to a similarly coated PET film.

TABLE 1

Property	Units	PENBB	PET
Tensile Strength MD TD	(MPa)	240 180	} 100-200
Elongation At Break MD TD	(%)	25 20	} 50
Tensile Modulus MD TD	(GPa)	9.2 8.0	} 4-6
UV resistance	% retained tensile strength	77	0
Shrinkage (at 150°C for 15 minutes) MD TD	(%)	0.3 0.3	> 1.0 > 1.0

As is evident from the above table, stiffness (tensile modulus) elongation at break, tensile strength, shrinkage and UV resistance are improved as compared to similarly coated PET films.

- 5 The film produced according to the above example is tested for reprographic adhesion as set forth above and provides greater than 95 percent adhesion as compared with a control uncoated polyester film which exhibited 0 percent adhesion.

## THAT WHICH IS CLAIMED IS:

1. Primer coated, biaxially oriented self-supporting mono- or multilayer copolyester film, wherein the copolyester is PENBB and wherein the primer coating contains a vinyl acetate copolymer.  
5
2. Primer coated biaxially oriented copolyester film according to Claim 1, wherein the primer coating consists essentially of a halogen-free copolymer of at least about 50 percent by weight of polymerized vinyl acetate, from  
10 about 1 to about 15 percent by weight of a copolymerized functional-group-containing comonomer which in the copolymerized state is capable of intermolecular crosslinking by the application of heat.
3. Primer coated biaxially oriented copolyester film according to Claim 1  
15 or 2, wherein the primer coating contains from about 0 to 49 percent by weight of one or more halogen-free mono-ethylenically unsaturated copolymerized monomers.
4. Primer coated biaxially oriented copolyester film according to Claim 2  
20 or 3, wherein said functional group present in said functional-group-containing comonomer is selected from the group consisting of amine, amide, acid anhydride, N-methylol, carboxyl, hydroxyl, epoxy and isocyanate.
5. Primer coated biaxially oriented copolyester film according to Claim 2,  
25 3 or 4, wherein said functional-group-containing comonomer is selected from the group consisting of N-methylolacrylamide and N-methylolmethacrylamide.
6. Primer coated biaxially oriented copolyester film according to any one  
30 or more of the preceding claims, wherein the coating is applied on one surface of the film.

7. Primer coated biaxially oriented copolyester film according to any one or more of claims 1-5, wherein the coating is applied on both surfaces of the film.
- 5 8. Primer coated biaxially oriented copolyester film according to any one or more of the preceding claims, wherein the film is a monolayer film.
9. Primer coated biaxially oriented copolyester film according to any one or more of the preceding claims, wherein the film has a birefringence of < 0.2.
- 10 0.2.
10. Primer coated biaxially oriented copolyester film according to any one or more of the preceding claims, wherein the PENBB polymer of the film has an IV > 0.5 dl/g.
- 15 11. Use of the primer coated biaxially oriented copolyester film according to claim 1 as a packaging film.
12. Use of the primer coated biaxially oriented copolyester film according to claim 1 as a reprographic film.
- 20

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10685**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B32B 33/00; DO6N 7/04

US CL :428/141, 143, 145, 147, 323, 325, 446, 480, 910

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/141, 143, 145, 147, 323, 325, 446, 480, 910

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,568,599 (ONO) 04 FEBRUARY 1986, entire document.	1-3
Y	US, A, 4,619,869 (KIRIYAMA) 28 OCTOBER 1986, entire document.	1-3
Y	US, A, 4,833,024 (MUELLER) 23 MAY 1989, entire document.	1-3
Y	US, A, 5,096,773 (SAKAMOTO) 17 MARCH 1992, entire document.	1-3

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

24 FEBRUARY 1993

Date of mailing of the international search report

13 APR 1993

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10685

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 11 & 12  
because they relate to subject matter not required to be searched by this Authority, namely:  
  
Claims 11 & 12 are directed to a "USE" PCT Article 17(2)(a)(i). "Use" claims not in method terminology is not search by this ISA.
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-10  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.  
☐ No protest accompanied the payment of additional search fees.